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## CHEMICAL SCIENCES

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# Canadian Journal of Research

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## THE DETONATION VELOCITY OF AXIALLY CAVITATED CYLINDERS OF CAST DINA<sup>1</sup>

M. KIRSCH,<sup>2</sup> G. PAPINEAU-COUTURE,<sup>3</sup> AND C. A. WINKLER

### Abstract

A method is described, involving the use of the Jones and Lamson Pedestal Comparator, for estimating velocities of detonation from the photographic record obtained on a rapidly moving film. The increase in detonation velocity in cavitated charges is accompanied by the appearance of a luminous effect which moves down the cavity approximately 1.6 times faster than the detonation wave. Both the luminous effect and the increase in detonation velocity disappear when the cavity is filled with water.

### Introduction

During 1944-45, the authors, in collaboration with Mr. M. C. Fletcher, assumed responsibility for installing and testing a high speed camera at the Explosives Research Laboratory of the National Research Council, Ottawa. Upon completion of the installation, the brief study reported in the present paper was made to provide a test of its operational stability and general suitability for research purposes. No claim to originality is made in studying detonation velocities in cavitated charges, nor is the present study regarded as more than a minor contribution in such studies. The results, however, would seem to be of sufficient interest to place on record.

### Experimental

#### *Apparatus*

The high speed rotating drum camera used in photographing the detonations was essentially the same as that described by Cairns (1). The image of the explosive was focused on a slit that was only one sixty-fourth of an inch away from a strip of 35 mm. film carried in the inside rim of a rapidly rotating drum. With a charge hanging vertically and detonated at the top, the luminosity moved down the explosive as the film moved across the slit. The photograph obtained, was therefore, a line slanted across the film. Where the detonation velocity was constant, the line was perfectly straight. Knowledge of the angle that this line makes with the perpendicular to the edge of the film,

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the magnification factor for the lens system, and the linear speed of the film permitted calculation of the rate of progress of the luminosity. A correction was necessary for the deviation of the slit image from perpendicularity to the edge of the film.

The required measurement of angles was made with a Jones and Lamson Pedestal Comparator, which consisted of a large ground glass disk on which was projected a magnified image of the film. Two perpendicular diameters were etched in the face of the disk, which could be rotated by a rack and pinion arrangement. The velocity of the luminosity was given by

$$V = \frac{d}{M(\tan \theta - \tan A)},$$

where  $V$  = the velocity of the luminosity in meters per second;

$d$  = the linear velocity of the drum in the camera in meters per second;

$M$  = the magnification factor for the lens system,  
= image/object;

$\theta$  = the angle which the straight line luminous trace makes with the vertical;

$A$  = the angle between the slit image and the vertical.

By diaphragming the drum camera to  $f$ -16 and developing the film in a highly alkaline developer, Eastman D-8, diluted 2 : 1, very sharp negatives were obtained, and the reading error in measuring the detonation velocity was only 0.2%.

#### *Preparation of Charges*

DINA (*bis*-( $\beta$ -nitroxyethyl)nitramine) was used in the investigation of cavitated charges since it was easily cast free of inner cracks, and its translucence facilitated the examination of the luminous effect within the cavity.

To prepare a cavitated charge, the crystalline DINA was melted in a steam bath and allowed to cool to 70° C. before casting. The mold consisted simply of a 10-in. long glass tube of appropriate diameter into which fitted a smaller tube held in a concentric position at both ends with two carefully bored stoppers. With one of the stoppers removed, the annular space between the two glass tubes was almost filled with liquid DINA, and the stopper replaced to ensure that the inner and outer tubes were concentric. The charge was half immersed in running water at about 10° C., the other half being cooled in air. The crystallization caused considerable decrease in volume and when the solidification had proceeded far enough to fix the inner tube in position, but before the top of the DINA had crystallized, the tube was refilled with liquid DINA. This process was continued until the tube was completely filled with explosive, care being taken always to pour the DINA before the melt had crystallized completely. In this way irregularities within the charge were minimized.

When the entire charge had crystallized, it was clamped vertically, and hot water (at *ca.* 60° C.) was run down the inner tube to melt a thin film of DINA (m.p. 52° C.) so that the inner tube could be removed. (Steam was used to remove the inner tube when its diameter was 3.2 mm.) A bare charge was prepared from a charge confined in glass by rotating the latter under hot running water to loosen the outer tube and permit its removal.

The density of all the DINA charges used in the present investigation, determined simply by measuring the volume of water displaced by the charge of known weight, was found to be constant at 1.60 gm. per ml. Moreover, since the detonation velocities of the full charges were reproducible within 0.2%, which was approximately the magnitude of the error in reading the angle of the detonation trace, the packing density was evidently sufficiently constant not to affect the detonation velocity.

In preparing a water-filled charge, one end of the cavity was plugged with DINA, a fine tube was inserted to the bottom of the cavity, and water was poured through it into the hole until several drops of water overflowed at the top of the charge, to eliminate all air bubbles.

To all the charges were attached a booster of plastic explosive and a 10-gm. or 25-gm. tetryl pellet. A thin layer of plastic explosive was placed between the DINA and the tetryl pellet to improve the contact between them, and the No. 8 electric blasting cap fitted into a hole in another wad of plastic explosive placed above the tetryl, the whole booster being attached to the charge with cellulose tape.

## Results

### *Effect of Polymorphism on Detonation Velocity*

One apparent disadvantage to the use of DINA in a study of detonation velocity is that it may exist in either of two polymorphic forms. Immediately after casting, the charges were distinctly yellow, but after standing in air at room temperature for several days, the color gradually changed to almost pure white. The method of casting was such as to favor the initial formation of the  $\beta$ -polymorph, and the solid-solid transformation to the room temperature stable  $\alpha$ -form was then characteristically slow. A series of experiments indicated that the detonation velocity was the same for both of the DINA polymorphs likely to crystallize under the casting conditions; the results are given in Table I.

TABLE I  
EFFECT OF POLYMORPHISM ON DETONATION  
VELOCITY, 22 MM. DIAMETER BARE CAST DINA

Crystal form	Detonation velocity m./sec.
$\alpha$	7770
Mixture $\alpha$ and $\beta$	7790
$\beta$	7779
$\beta$	7738

Since the density of the charges was constant, and the polymorphism apparently did not complicate the characteristic detonation velocity of DINA, no special precautions were necessary in the preparation of charges for the investigation of the effect of cavitation on the rate of detonation.

#### *Confined Cavitated Charges*

Experiments with cylindrical charges of cast DINA, with axial cavities of various diameters, confined in glass tubes indicate the variation of detonation velocity with cavity size. The results are given in Table II, and two typical photographs are reproduced in Plate I, showing the cavity luminosity travelling to the right of, i.e., ahead of, and much faster than, the detonation wave. The data indicate that the rate of detonation decreases continuously with increasing cavity diameter beyond the smallest used in the present study.

TABLE II  
CAVITATED DINA CONFINED IN GLASS

Diameter of cavity, mm.	Number of charges	Mean detonation velocity, m./sec.	Average deviation, m./sec.
(a) Charge diameter = 16 mm.			
0	4	7798	14
3.2	3	8065	9
4.2	3	8019	18
7.5	4	7707	28
9.9	3	7724	44
(b) Charge diameter = 22 mm.			
0	5	7844	6
3.2	3	8337	71
7.5	3	8093	13
12.6	3	7972	33
15.2	2	7818	37

#### *Unconfined Cavitated Charges*

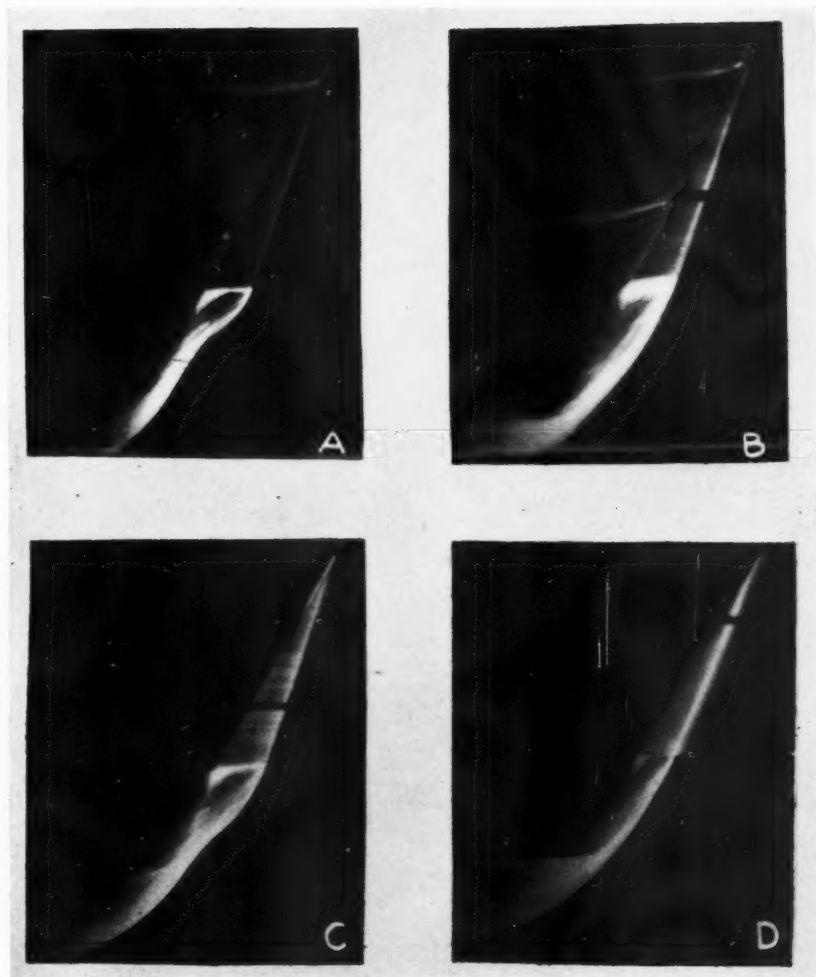
The measured detonation velocities of unconfined charges are given in Table III, and two typical photographs are reproduced in Plate I. The same qualitative variation in the rate of detonation is observed in the bare as in the confined charges.

#### *Water-filled Charges*

Charges in which the cavities were filled with water were fired immediately after preparation to minimize the loss of liquid by seepage through the walls of the explosive. The detonations were much less luminous than those obtained with air-filled cavities. The numerical results indicate that the



PLATE I



*Rate photographs of 16 mm. diameter charges with axial cavities. Unconfined, A, 3.2 mm. cavity; B, 7.5 mm. cavity. Confined, C, 4.2 mm. cavity; D, 9.9 mm. cavity.*

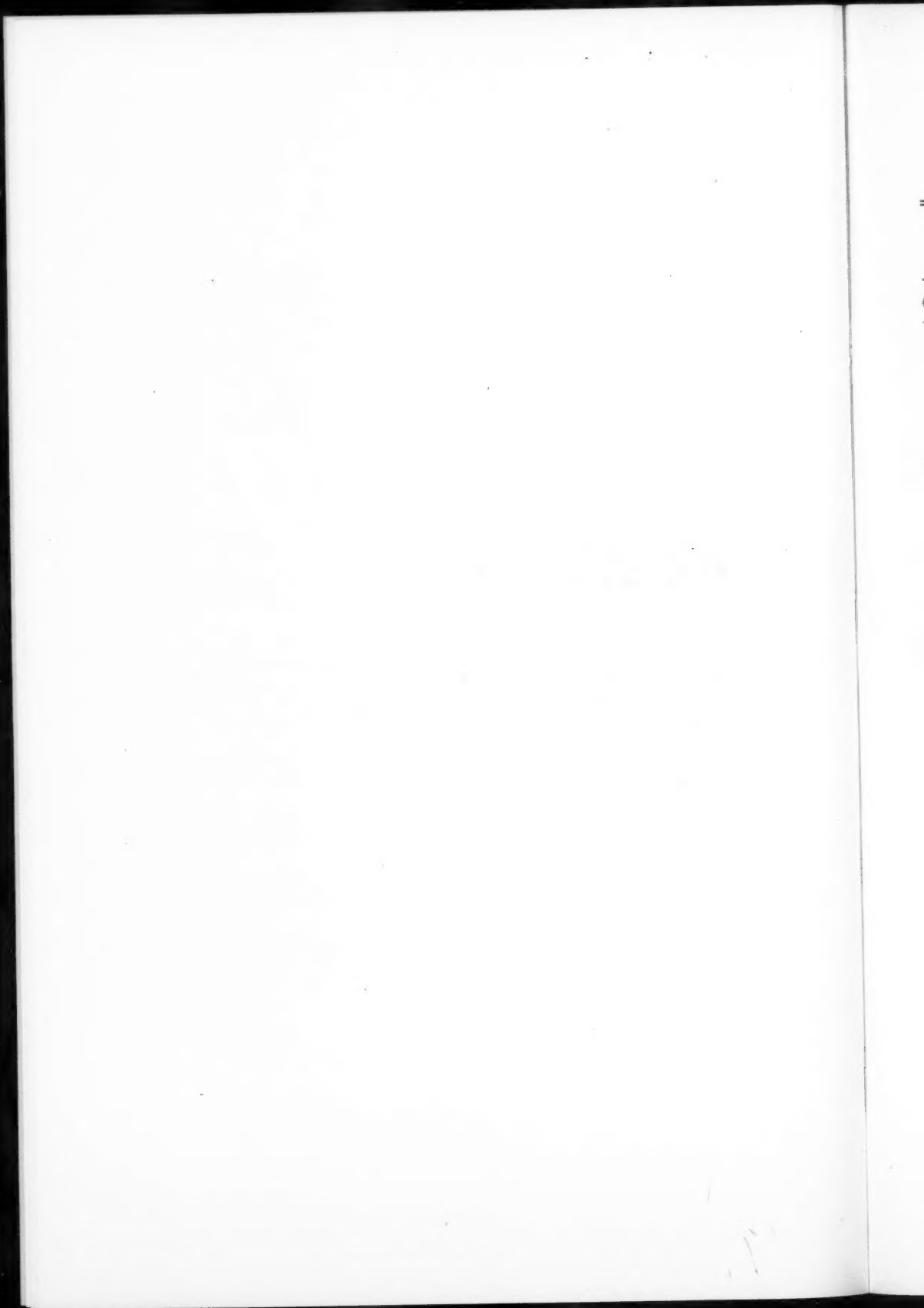




TABLE III  
UNCONFINED CAVITATED DINA

Diameter of cavity, mm.	Number of charges	Mean detonation velocity, m./sec.	Average deviation, m./sec.
(a) Charge diameter = 16 mm.			
0	3	7753	15
3.2	4	8021	82
4.2	4	7993	47
7.5	4	7886	32
9.9	2	7757	19

(b) Charge diameter = 22 mm.

0	5	7776	17
3.2	2	8190	190
7.5	3	7989	22
12.6	3	7797	10
15.2	3	7593	13

water apparently reduces or eliminates entirely the increase in detonation velocity caused by an air-filled cavity, and the photographs showed that the luminous effect within the cavity disappeared when water was present.

TABLE IV  
WATER-FILLED CAVITATED DINA CONFINED IN GLASS

Diameter of cavity, mm.	Number of charges	Mean detonation velocity, m./sec.	Average deviation, m./sec.
(a) Charge diameter = 16 mm.			
3.2	3	7865	22
4.2	3	7792	12
7.5	3	7812	20
9.9	2	7772	23
(b) Charge diameter = 22 mm.			
3.2	2	7911	24
7.5	2	7828	0
12.6	2	7871	16
15.2	2	7767	51

### Discussion of Results

The results to be explained may be logically divided into two main groups only indirectly related to each other:

1. The cause of the luminous effect in the cavity,
2. The effect of cavitation on the observed detonation velocity.

Since the detonation of the explosive results in a large pressure rise at the surface of the cavity, a shock wave travels inward from the walls. It is reasonable to assume that the interaction of shock waves thus formed occurs by a process comparable to the Mach reflection of plane waves (giving rise to the Munroe effect) resulting in a 'Mach' wave of greatly increased amplitude moving down the axis at a rate greater than the detonation rate.

This hypothesis may explain satisfactorily the results previously described.

The increase in detonation velocity observed in cavitated charges disappears when the cavity luminosity is eliminated by filling the cavity. It appears, therefore, that this increase is attributable to the presence of the high speed cavity disturbance. Since the disturbance does not initiate detonation the increase in detonation rate in axially cavitated charges must be due to the disturbance presensitizing the explosive ahead of the detonation wave.

The wave resulting from shock interaction in a dense medium such as water would have a smaller amplitude and velocity. It is unlikely that the velocity of such a wave would be greater than the detonation velocity, hence no presensitization could occur in a water-filled cavity.

### Acknowledgment

The authors gratefully acknowledge the co-operation of Dr. J. S. Tapp whose continued interest in the work was greatly appreciated.

### Reference

1. CAIRNS, R. W. *Ind. Eng. Chem.* 36 : 79. 1944.

# STUDIES ON THE ELECTRO-OXIDATION OF TETRAVALENT URANIUM<sup>1</sup>

By R. H. BETTS

## Abstract

The conversion of uranous ion to uranyl ion at a platinum anode has been studied over a wide range of current densities and anode potentials. At high current densities, the rate of the oxidation is dependent on the uranous ion concentration and is independent of the particular current density used. At low current densities, the rate of the process increases exponentially with increases in the anode potential and temperature, but is independent of the uranyl ion concentration. It is concluded that at high current densities, the rate of oxidation is limited by the rate of diffusion of uranous ion to the anode, while at low current densities, the rate of the reaction is limited by the slowness in electron transfer between the metallic ion and the anode. A formal correlation is made between the irreversible characteristics of this system and those displayed during the electrodeposition of hydrogen and oxygen from aqueous solution.

## Introduction

There are very few references in the literature to processes involving the anodic oxidation of uranium ions. The polarographic studies made by Heal (8, 9, 10) showed that trivalent uranium,  $U^{III}$ , may be oxidized reversibly to tetravalent uranium  $U^{IV}$  at a dropping mercury electrode, the standard redox potential for the reaction being  $-0.75$  v.\* However, no evidence for reversible processes involving  $U^{IV}$  and either  $U^V$  or  $U^{VI}$  could be found.

Polarographic experiments made by Heal at high positive potentials with a platinum microelectrode gave evidence of some slight irreversible oxidation of  $U^{IV}$  (8, 9, 10). An oxidation process, in the presence of  $U^{IV}$ , began at a potential nearer to the reversible oxygen electrode than it did in solutions of the base electrolyte alone (6 *N* sulphuric acid). Heal attributed this effect to the depolarizing action of  $U^{IV}$ , in which the metallic ion was oxidized by 'nascent' oxygen. The current-potential relations were rather ill-defined in these experiments.

Plutonium, which is an actinide element similar to uranium in many of its chemical properties (7), also undergoes electro-oxidation in aqueous solution. Fig. 1, which is taken from unpublished work by the present writer, shows the current-potential relation for  $Pu^{IV}$  perchlorate in 1.0 *N* perchloric acid, using a platinum microelectrode. This result indicates that irreversible oxidation of  $Pu^{IV}$  occurs in regions of sufficiently high positive potential (1.4 to 1.6 v.). (The wave-form at  $+0.90$  v. in Fig. 1 is typical of a reversible reaction and represents the reduction of  $Pu^{IV}$  to  $Pu^{III}$ . This  $Pu^{IV} - Pu^{III}$  wave has already been described in the literature (7).)

<sup>1</sup> Manuscript received January 12, 1948.

Contribution from Chemistry Branch, Atomic Energy Project, National Research Council, Chalk River, Ontario. Issued as N.R.C. No. 1606.

\* All values of the potential are given with reference to the normal hydrogen electrode, using the European sign convention.

The present work was undertaken as the first in a series of detailed investigations of electro-oxidation phenomena among the actinide elements. In this paper, a closer examination of the electro-oxidation of  $U^{IV}$  has been made.

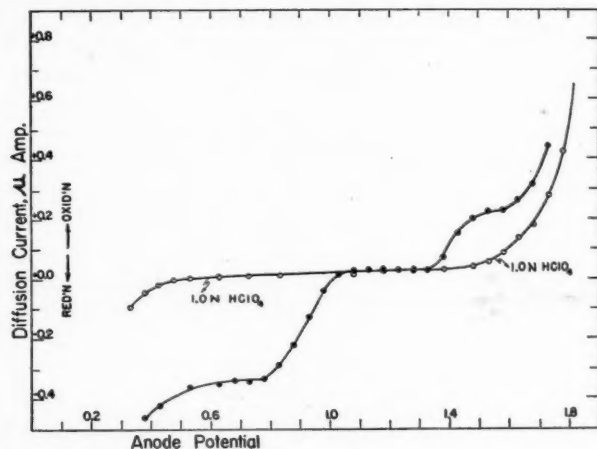


FIG. 1. Polarogram of 0.003 M plutonium perchlorate in 1.0 M perchloric acid.

The current-potential ( $i$ - $V$ ) relations for the oxidation of  $U^{IV}$  have been examined over a wide range of current densities (C.D.), and the current efficiency (C.E.) over a somewhat smaller current density range. However, before a detailed description of the experimental methods and results is presented, a short account will be given of relevant anodic processes.

Glasstone and Hickling have reviewed the experimental results for a considerable number of electrolytic oxidations, including  $Cr^{III} - Cr^{VI}$ , iodate-periodate, and a variety of organic molecule couples (4). Unfortunately, most of this work was done at relatively high current densities, where the main electrochemical process was the deposition of oxygen. Further, the range of current densities examined was rather limited (*ca.* 100-fold). In addition, no clear distinction was made between the various causes of overpotential. Glasstone and Hickling concluded that the  $i$ - $V$  relations were in general merely those involved in the electrodeposition of oxygen.

Bowden and Agar (2), in a review of irreversible electrode processes, have distinguished several causes of irreversibility of which two are discussed briefly below.

#### (1) Activation Overpotential

The electrode process may occur in several stages, each with an associated energy of activation. The reaction velocity will be controlled by that stage having the highest energy of activation. It may be expected that the activation energy will be some function,  $\alpha$ , of the electrode potential. For oxidation processes in general, an increase in the anode potential will lower the energy

of activation of this slowest stage. If  $W$  joules is the energy of activation of the slowest step at an arbitrary potential  $V_0$ , then the energy of activation will be  $(W - \alpha VF)$  at  $V$  volts removed from  $V_0$ .  $F$  is the Faraday constant. For many reactions,  $\alpha$  is a constant. Further, if the energy distribution among the reacting species is Maxwellian, then the number of ions reacting per second,  $n$ , at  $V$  volts will be proportional to

$$N_0 e^{-(W - \alpha VF)/RT}, \quad (1)$$

where  $N_0$  is the concentration of ionic species at the electrode surface,  $R$  is the gas constant, and  $T$  the temperature. The current density gives a measure of  $n$ , and therefore

$$\ln i = K - \frac{W}{RT} + \frac{\alpha VF}{RT}, \quad (2)$$

i.e., a plot of  $\ln i$  vs.  $V$  should yield a straight line if the rate of the reaction is limited by energy of activation considerations. The  $i$ - $V$  relations for electrodeposition of oxygen and hydrogen are of this kind (2).

#### (2) Concentration Overpotential

The second cause of overpotential is linked with concentration changes that occur at the electrode during passage of the current. (This effect is also known as concentration polarization.) When an electrochemical process has reached a steady state, the rate of depletion of ions at the electrode surface is equal to the rate at which ions are supplied from the bulk of the solution. For solutions containing a relatively large concentration of indifferent electrolyte, ions are supplied to the electrode surface mainly by diffusion; the rate of linear diffusion can then be calculated from the concentration gradient existing at the electrode surface, and the diffusion coefficient of the ion (2):

$$i = \frac{(C_0 - C_e)DF}{d}. \quad (3)$$

In this expression,  $D$  is the diffusion coefficient of the ion in square centimeters per second,  $(C_0 - C_e)$  is the change in concentration of the oxidizable ion over a distance  $d$  from the electrode surface, and  $F$  is the Faraday constant. The factor  $d$  in Equation (3) represents the thickness of the diffusion layer. In unstirred solutions,  $d$  has a value in the vicinity of 0.05 cm., and under conditions of violent stirring it may reach a value of 0.001 to 0.005 cm. (2). In Equation (3) above, if  $C$  is expressed in gm. equivalent per cm<sup>3</sup>,  $i$  represents current density in amp. per cm<sup>2</sup>.

Further, it is clear that the maximum concentration gradient cannot exceed  $C_0/d$ , when the concentration of oxidizable ion at the electrode surface is zero. Under these conditions, the limiting diffusion current is given by

$$i_d = \frac{C_0 DF}{d} \text{ amp. per cm.}^2 \quad (4)$$

It follows that the maximum rate of diffusion should be a linear function of the concentration of the reacting species. If the current density is made to

exceed this limiting value, a second process must occur, with a concomitant abrupt rise in potential. For systems we are concerned with here, this will involve the electrodeposition of oxygen.

### Experimental

#### *Apparatus and Methods*

The electrolytic apparatus consisted simply of two 100 ml. beakers that were connected by a removable U-tube. Plugs of filter paper in the open ends of the tube effectively prevented mixing of the anolyte and catholyte. A rectangular sheet of platinum, of 3.0 sq. cm. apparent area, was used as the anode. It was attached to the end of an air-driven shaft, and mounted vertically above the anode compartment. During electrolysis, this electrode could be rotated at 300 to 500 r.p.m. if desired. A stationary platinum cathode was used. Current was supplied from two 6 v. batteries through a rheostat and milliammeter. Measurements of low current densities were made by the standard resistance-potentiometer method.

A saturated calomel electrode (S.C.E.) was used as a reference electrode for measurement of anode potentials. It was connected with the anode compartment by a second U-tube filled with perchloric acid, with an intervening solution of 1 *N* hydrochloric acid between the saturated calomel electrode and the bridge. To minimize resistance overpotential errors (2), a capillary tip was sealed to the end of the U-tube, and pressed lightly against the anode. Potentials were measured by a vacuum-tube voltmeter, sensitive to  $\pm 1$  mv. Junction potentials were virtually constant for all experiments, and so have been ignored.

To secure as reproducible a surface as possible for each experiment, the anode was cleaned successively in hot chromic acid and water, and then heated to redness in a flame before each experiment.

Tetravalent uranium was supplied from a stock solution of uranous sulphate in 1.0 *N* perchloric acid. The  $U^{IV}$  content was checked frequently by titration of an aliquot with standard potassium permanganate. Perchloric acid (1.0 *N*) was used as the electrolyte.

The experimental procedure for measurement of current efficiency was as follows: suitable volumes of perchloric acid were pipetted into the anode and cathode compartments, and the U-tube filled with the same acid and inserted in place. The external rheostat was adjusted to give the required current density, and then  $U^{IV}$  added to the anolyte at zero time.

After the oxidation, the anode compartment was removed, and the residual  $U^{IV}$  determined by titration with standard potassium permanganate. Titration of the bridge solution and catholyte in several experiments showed that less than 1% of the  $U^{IV}$  migrated from the anode compartment during the electrolysis. Simultaneous oxidation by air of  $U^{IV}$  was found to be small (1 to 2%) in 1.0 *N* acid, and was generally neglected in calculation of current efficiencies.



However, for several experiments, where the time of electrolysis was long, this factor was somewhat larger, and appropriate corrections were therefore applied.

Measurements of current efficiency were reproducible to 1%, and were calculated on the basis that 96,500 coulombs is equivalent to 119.0 gm. of uranium.

The procedure used for measurement of anode potentials was as follows: The largest current to be used in an experiment was passed through the cell until the anode potential attained a constant value.  $U^{IV}$  was then added to the anode compartment, and the current density was changed successively to smaller values. Simultaneous readings of current and potential were taken at each value of the current density. The potential became constant within a minute or two after each change in the current.

### Experimental Results and Discussion

#### A. MEASUREMENTS OF CURRENT EFFICIENCY IN STIRRED SOLUTIONS

##### (1) Effect of $U^{IV}$ Concentration

The effect of  $U^{IV}$  concentration on current efficiency is shown in Fig. 2. These experiments were made at a current density of 4.90 ma. per  $cm^2$ . The concentration of  $U^{IV}$  changed as the reaction proceeded, and so the arithmetic

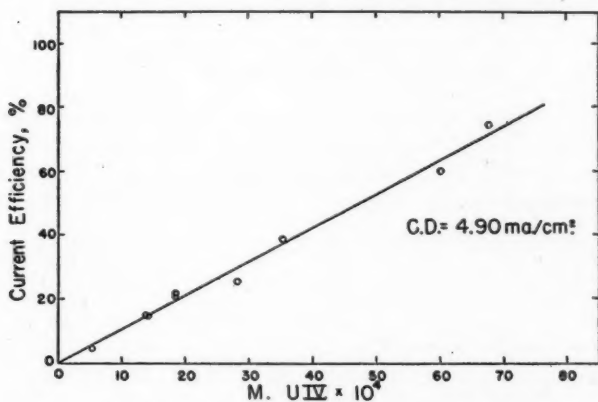


FIG. 2. Effect of uranium concentration on current efficiency.

mean of the initial and final concentrations has been taken in each case. The current efficiency is a substantially linear function of the  $U^{IV}$  concentration in the range examined; as indicated earlier, this is to be expected for a diffusion-controlled process.

##### (2) Effect of Current Density

The current efficiency of the oxidation is affected markedly by the current density used, and increases rapidly as the current density is decreased



(Table I). To make the results comparable, the average concentration of  $U^{IV}$  for each experiment was maintained as nearly constant as possible at *ca.* 0.2 mgm. per ml.

TABLE I  
EFFECT OF CURRENT DENSITY ON EFFICIENCY OF OXIDATION OF  $U^{IV}$

Average conc. $U^{IV}$ , $M \times 10^4$	Current density, ma./cm <sup>2</sup>	Current efficiency, %
8.6	1.23	59.2*
7.5	2.47	20.7
8.6	4.95	15.5
11.1	9.90	7.7
8.0	15.3	2.2

\* Corrected for oxidation by air.

These results may be accounted for as follows: The measured current density is the sum of two reactions, which may be written formally as



The current efficiency of the process (for  $U^{IV}$  oxidation) is then

$$\frac{\text{Reaction (b)}}{\text{Reaction (a)} + \text{Reaction (b)}} \times 100\%. \quad (5)$$

The maximum rate of Reaction (b) may be calculated from Equation (4) discussed earlier. In the absence of exact data, a value of  $1 \times 10^{-8}$  cm<sup>2</sup>. per sec. has been assumed for the diffusion coefficient of  $U^{IV}$ . This appears to be a not unreasonable value, in view of similar values reported for the uranyl

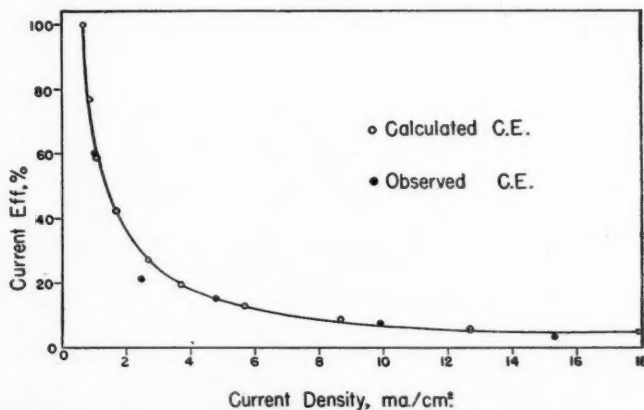


FIG. 3. Effect of current density on the current efficiency for oxidation of uranium.

ion (6) and for other metallic ions (3). For stirred solutions, the limiting diffusion current,  $i_d$ , for a concentration  $C_0$  of  $U^{IV}$  then has a value of  $400 C_0$  amp. per  $cm.^2$ . These relations have been used to calculate the theoretical current efficiency for the experiments listed in Table I. The results, given in Fig. 3, show good agreement between the calculated and experimentally determined current efficiencies, and indicate that at high current density, the rate of the oxidation of  $U^{IV}$  is limited by the rate of diffusion of  $U^{IV}$  to the electrode surface. The current-anode potential relations described below give further confirmation of this point of view.

## B. MEASUREMENT OF ANODE POTENTIALS

### (1) Oxygen Overpotential

The current-potential relations for electrodeposition and electrosolution of oxygen on a platinum electrode from a solution of 1.0 *N* perchloric acid are shown in Fig. 4. The  $i$ - $V$  relation for the electrosolution of oxygen was obtained by measurement of potential and current density with the battery and milliammeter connected in the opposite direction to that used for the electrodeposition experiments. The electrode had been polarized anodically before these measurements were made, and, consequently, the electrolyte was saturated with oxygen. These relations were unaffected by stirring of the solution, a result that is characteristic of activation overpotential phenomena (2).

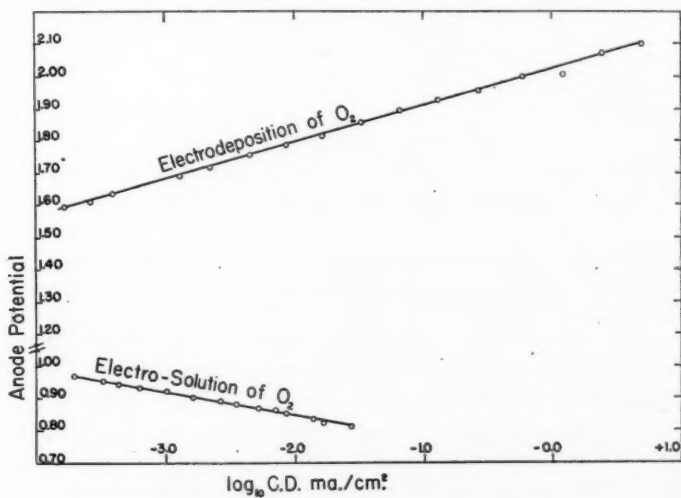


FIG. 4. Current-potential relations for electrodeposition and electrosolution of oxygen.

The slope of the  $\log i$ - $V$  line for deposition of oxygen is 112 mv. for a 10-fold change in current density. This agrees well with the value of 116 mv. reported by Bowden for 0.2 *N* sulphuric acid solutions (1, 2). Extrapolation

of the electrosolution and electrodeposition lines to intersection (not shown in Fig. 4) yields a value of +1.17 v. for the reversible oxygen electrode. This is in good agreement with the value of +1.23 v. calculated from thermodynamic data (11).

## (2) Anode Potentials in the Presence of $U^{IV}$

The  $i$ - $V$  relations in *unstirred* solutions of 1.0 *N* perchloric acid containing varying amounts of  $U^{IV}$  are shown in Fig. 5. These results were obtained at 18.1°C. At high current densities, they coincide with that for 1.0 *N*

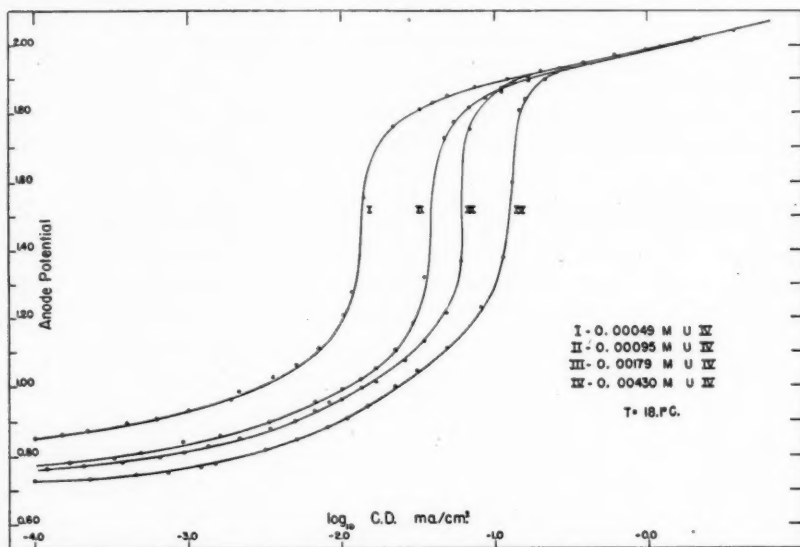


FIG. 5. Current-potential relations for electro-oxidation of uranium.

acid alone (Fig. 4). However, at lower current densities, the potential changes abruptly over a narrow range of current density to more negative values. For a given  $U^{IV}$  concentration, the value of the current density at this sharp inflection point agrees with the limiting diffusion current calculated from Equation (4), and is displaced in an approximately linear fashion with changes in  $U^{IV}$  concentration (Table II).

It is evident that the value of the current density in this region may be identified with the maximum rate of diffusion of  $U^{IV}$  to the electrode surface. Slight increases in the current density above this limiting value result in this deposition of oxygen, and the potential rises rapidly to the value determined by the kinetics of the oxygen electrode.

The effect of stirring is to decrease the effective thickness of the diffusion layer, with a consequent increase in the value of the limiting diffusion current (Fig. 6).

At current densities approximately 10-fold less than the limiting current, and lower, the  $i$ - $V$  relation is similar in form to that for electrodeposition of oxygen, i.e., an approximately linear relation between  $\log i$  and  $V$  is found.

TABLE II  
COMPARISON OF THEORETICAL AND OBSERVED LIMITING  
DIFFUSION CURRENTS FOR OXIDATION OF  $U^{IV}$

$M U^{IV} \times 10^4$	$i, \text{ma./cm.}^2$	
	Observed	Calculated
4.9	0.014	0.019
9.5	0.037	0.037
17.9	0.065	0.067
43.0	0.13	0.16

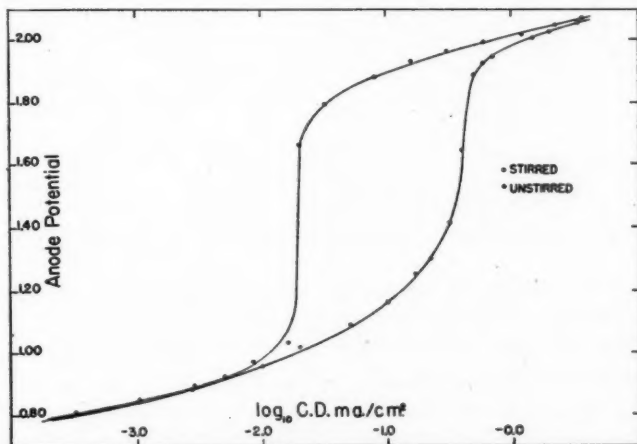


FIG. 6. Effect of stirring on current-potential relations for oxidation of uranium.

Moreover, the  $i$ - $V$  relations in this region, in contrast to those at intermediate current densities, are substantially unaffected by stirring (Fig. 6). These results indicate that at low current densities the rate of the oxidation is not limited by a diffusion-controlled process, and that an activation overpotential mechanism is operative. A more quantitative formulation of the  $\log i$ - $V$  relations will be deferred until consideration is given to concentration polarization effects (*vide infra*).

The effect of changes in temperature on the  $i$ - $V$  relation is shown in Fig. 7. These results were obtained with a stationary anode in a solution 0.00092  $M$  in  $U^{IV}$ . A rise in temperature increases both the rate of oxidation of  $U^{IV}$  and the rate of oxygen deposition. The shift in the limiting diffusion current

appears to be somewhat larger than would be expected for a diffusion-controlled process (2, 13). It is possible, however, that the additive effects of small increases in the diffusion coefficient, decreases in the thickness of the diffusion

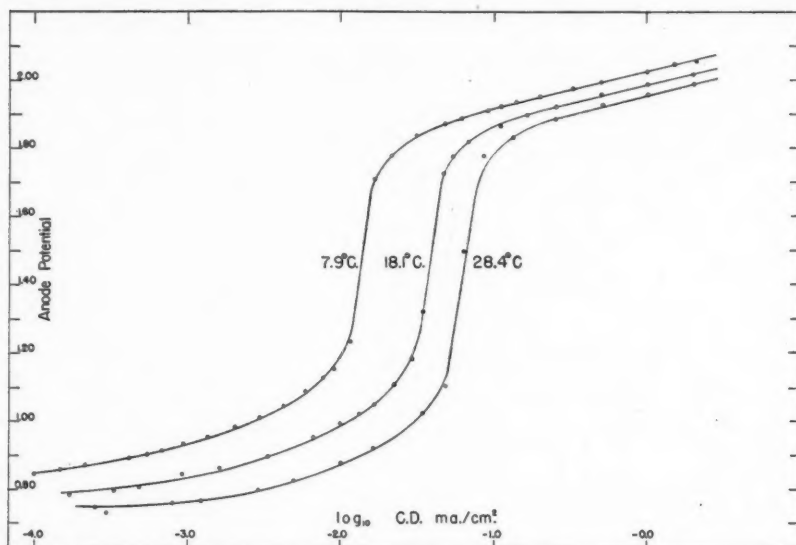


FIG. 7. Effect of temperature on current-potential relations for oxidation of uranium.

layer, and a decrease in the viscosity of the anolyte, together with increased convection currents at the higher temperatures, are sufficient to account for the increase in the rate of diffusion of  $U^{IV}$  to the electrode surface.

#### Concentration Overpotential Effects

It is evident that at zero polarizing current, the concentration of  $U^{IV}$  at the electrode surface ( $C_e$ ) is the same as for the bulk of the solution ( $C_0$ ). When the polarizing current is equal to the limiting diffusion current,  $i_d$ ,  $C_e$  has a value of zero. Hence the value of  $C_e$ , and consequently the degree of concentration polarization, varies continuously as the current density is changed between these limits. The ratio  $\frac{C_e}{C_0}$  may be evaluated by a suitable combination of Equations (3) and (4) above to give

$$\frac{i}{i_d} = 1 - \frac{C_e}{C_0} \quad (6)$$

For any current  $i$ , the value of  $C_e$  may be calculated by means of Equation (6), since  $C_0$  and  $i_d$  are known.

To calculate the concentration overpotential effects for the  $i$ - $V$  relations in Fig. 7, where the anode potential varies, and the  $U^{IV}$  concentration in the body of the solution is constant, it is also necessary to know the relation

between  $C_e$  itself and the anode potential. Accordingly, this relation was determined at 0.01 ma. per cm.<sup>2</sup> with  $U^{IV}$  concentration varying from 0.0015 to 0.0202 *M*. (Simple calculations of the type exemplified in Equation (6) show that under these conditions, concentration overpotential effects are negligible, i.e.,  $C_e = C_0$ .) The results of this experiment are shown in Fig. 8.

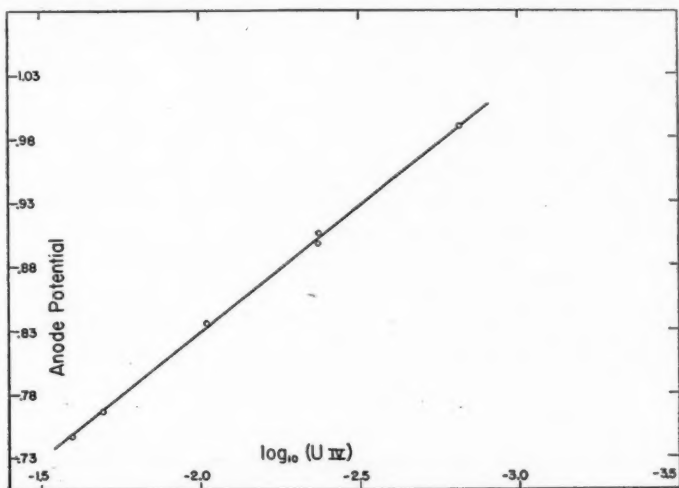


FIG. 8. Relation between anode potential and uranium concentration at a current density of 0.010 ma. per sq. cm.

The anode potential  $V$  was found to vary directly as the logarithm of the  $U^{IV}$  concentration, a 10-fold change in the latter causing a  $-0.198$  v. change in the potential.

This result, together with Equation (6), can be utilized to correct the observed  $i$ - $V$  relations for concentration overpotential effects. For example, when the current is 30% of the limiting diffusion current,

$$\begin{aligned} \frac{i}{i_d} &= 0.30 \text{ and } \frac{C_e}{C_0} = 0.70 \\ dV &= -0.198 \log \frac{C_0}{C_e} \\ &= -0.032 \text{ v.} \end{aligned}$$

At a current  $i = 0.30 i_d$  then, the value of the anode potential as determined from Fig. 7 is 0.032 v. more positive than it would be in the absence of concentration overpotential effects. Other current densities can be treated in a similar manner.

The results of such corrections on the shape of the  $i$ - $V$  relations determined at different temperatures are shown in Fig. 9. The magnitude of the correction is negligible at current densities less than one-tenth of the limiting diffusion current, but becomes increasingly significant as the current density approaches

the limiting diffusion current. The general effect of these corrections is to make  $\log i$  a more nearly linear function of  $V$ . It will be noted, however, that in regions of lowest anode potentials, the  $\log i$ - $V$  relation departs con-

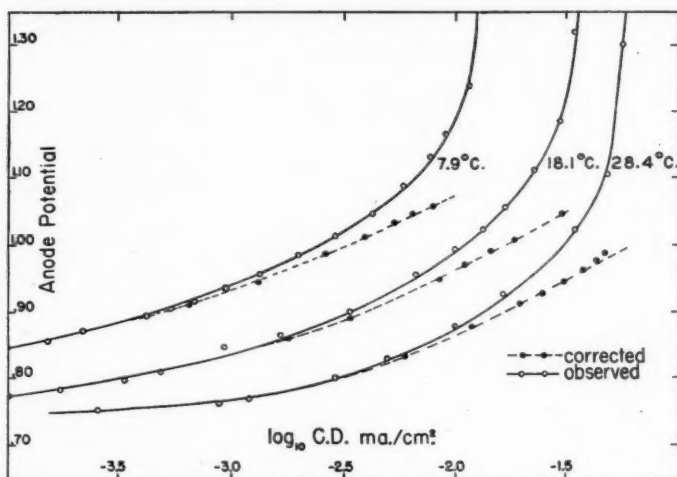


FIG. 9. Effect of concentration overpotential on current-potential relation for oxidation of uranium.

siderably from its linear form; this is attributed to the effect of the electro-solution of oxygen (cf. Fig. 4).

It is convenient at this point to develop more explicit relations between current density, ( $i < i_d$ ),  $V$ ,  $T$ , and  $U^{IV}$ . Following Bowden's treatment of activation overpotential phenomena (2), let  $W$  joules be the energy of activation, at 0.0 v. on the hydrogen scale, for the rate-controlling step in the oxidation of  $U^{IV}$ . An increase in the anode potential to  $V$  volts will decrease the energy of activation by an amount  $\alpha VF$ , where  $\alpha$  is a suitable constant that may be evaluated from the experimental data (for oxygen deposition,  $\alpha = 0.5$ ). If the energy distribution among the  $U^{IV}$  ions is Maxwellian, then the number of  $U^{IV}$  ions oxidized per second,  $n$ , will be proportional to

$$N_0 e^{-(W - \alpha VF)/RT}, \quad (7)$$

where  $N_0$  is the  $U^{IV}$  concentration at the electrode surface;  $n$  may be expressed in terms of current density, and  $N_0$  in terms of gram equivalents per liter:

and

$$i = K[U^{IV}] e^{-(W - \alpha VF)/RT} \quad (8)$$

or

$$\log_{10} i = K^1 + \log_{10} [U^{IV}] - \frac{1}{2.303 RT} [W - \alpha VF] \quad (9)$$

Several methods may be used to test the applicability of Equation (9) to the electro-oxidation of  $U^{IV}$ , at current densities below the limiting diffusion current.



(i) At constant  $U^{IV}$  concentration, a plot of  $\log i$  vs.  $V$  should yield a straight line, from the slope of which  $\alpha$  may be determined. The substantial linearity between  $\log i$  and  $V$  is shown in Fig. 9, from which the value of  $\alpha$  is  $0.36 \pm 0.02$ . It will be recalled that these curves have been corrected for concentration overpotential effects, and therefore represent  $\log i$ - $V$  relations at constant  $U^{IV}$  concentration.

(ii) At constant current density, a plot of  $\log [U^{IV}]$  vs.  $V$  should also give a straight line since it follows from Equation (9) that

$$\log_{10} [U^{IV}] = K'' - \frac{\alpha VF}{2.303 RT}. \quad (10)$$

We have seen already that such a relation applies (Fig. 8).

(iii) The apparent value of the energy barrier ( $W - \alpha VF$ ) in Equation (9) may be evaluated from the temperature coefficient of the overpotential (at constant current density):

$$\left( \frac{dV}{dT} \right)_i = - \left[ \frac{W - \alpha VF}{\alpha FT} \right], \quad (11)$$

or from the temperature coefficient of the current density (at constant  $V$ ):

$$\left( \frac{d \log i}{dT} \right)_V = \frac{W - \alpha VF}{2.303 RT^2}. \quad (12)$$

Equations (11) and (12) have been used to calculate the energy of activation at various current densities and anode potentials, using the data provided from the  $\log i$ - $V$  relations shown in Fig. 9. The results of these calculations are given in Table III.

TABLE III

COMPARISON OF ACTIVATION ENERGIES (CALCULATED BY DIFFERENT METHODS) FOR ELECTRO-OXIDATION OF  $U^{IV}$

Temperature range, °K.	Method of calculation				
	At const. V.			At const. C.D.	
	0.90 V	0.95 V	1.00 V	0.01 ma./cm. <sup>2</sup>	0.005 ma./cm. <sup>2</sup>
281 - 291	28.7	26.4	25.2	24.8	23.8
291 - 301	27.9	24.3	24.6	25.3	23.2

Values in kilogram-calories per mole.

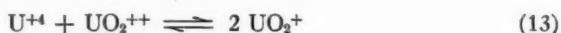
The agreement in the values of ( $W - \alpha VF$ ) obtained from the two methods of calculation, and also the agreement between the results for different temperature intervals, is further evidence that Equation (9) represents adequately the functional relations between  $U^{IV}$ ,  $i$ ,  $V$ , and  $T$ . It will, of course, be understood that Equation (9) refers only to those portions of the  $i$ - $V$  curves for which concentration overpotential effects are either negligible or can be taken into account.

*Hypotheses Regarding the Mechanism of the Reaction*

The essential similarity between the  $\log i$ - $V$  relations for electrodeposition of oxygen and hydrogen, on one hand, and those for the oxidation of  $U^{IV}$ , on the other, suggests that an analogous mechanism is operative in restricting the rate of all three reactions. The rate-controlling step in the first two reactions is thought to involve electron transfer; it has been demonstrated theoretically that provided the transfer of charge is the rate-controlling step, the rate of an electrochemical reaction should be an exponential function of the electrode potential (5). In view of these considerations, one may conclude that the rate of electron transfer between the  $U^{IV}$  ion and the anode is the rate-controlling step in the oxidation. Subsidiary hydrolytic reactions must intervene at some stage, of course, in order to proceed from  $U^{IV}$  to the  $U^{VI}$  oxy-ion. However, in view of the uncertain nature of the actual configuration of  $U^{IV}$  ion itself in solution, the exact sequence of electron transfers and hydrolytic reactions cannot be specified with any degree of certainty from the results of the present studies.

Other possible mechanisms may be considered briefly. It is very unlikely that oxidation of  $U^{IV}$  proceeds by a simple reaction between oxygen and the metallic ion, since at potentials below + 1.23 v. the rate of electrodeposition of oxygen is negligible compared with the observed rate of oxidation of  $U^{IV}$ . Moreover, the chemical stability of  $U^{IV}$  in acid solution to oxidation by air precludes this possibility (12).

The disproportionation reaction suggested by Heal (8, 9, 10) might conceivably provide a route for oxidation of  $U^{IV}$  to  $U^{VI}$ :

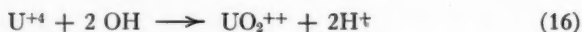


followed by



If such a mechanism contributes materially to the oxidation of  $U^{IV}$ , addition of  $U^{VI}$  to a solution of  $U^{IV}$  should shift Equilibrium (13) to the right, and permit a higher rate of oxidation of  $UO_2^{+}$ , and hence  $U^{IV}$ . However, experiments made in the present studies with mixtures of  $UO_2^{++}$  and  $U^{IV}$  showed that the presence of uranyl ion did not affect the rate of oxidation of  $U^{IV}$ . It is concluded that this mechanism plays no part in the oxidation process.

Another possibility is that  $U^{IV}$  is oxidized by hydroxyl radicals formed by the discharge of hydroxyl ions at the electrode surface:



Mechanisms of this type form a central feature of Glasstone's theories of irreversible anodic phenomena (4). There is, however, no direct evidence in the literature that hydroxyl radicals are formed as the first step in the electrodeposition of oxygen. Moreover, the free energy change for the formation of hydroxyl radicals from hydroxyl ions in aqueous solution is estimated to

be 33.8 kcal. (11). At potentials below  $+1.1$  v., the concentration of hydroxyl radicals in equilibrium with hydroxyl ions in  $1.0$  *N* acid solutions would be vanishingly small.

### Conclusion

The anodic oxidation of  $U^{IV}$  proceeds by a stepwise mechanism, the slowest stage of which involves electron transfer from the metallic ion to the anode. At the lowest anode potentials examined, the rate of electron transfer limits the over-all rate of the reaction. Increases in the anode potential decrease the activation energy of this stage, and the rate of the reaction increases in an exponential manner with the potential in this region. However, at sufficiently high potentials, the rate of diffusion of  $U^{IV}$  to the electrode surface becomes the rate-controlling step. Increases in the current density above the limiting rate of diffusion of  $U^{IV}$  result in the deposition of oxygen, and the anode potential rises to the value determined by the kinetics of the oxygen electrode. Evidence provided by current efficiency measurements shows that this rise in potential does not increase the rate of oxidation of  $U^{IV}$ . The rate of the reaction remains diffusion-controlled and is now independent of potential.

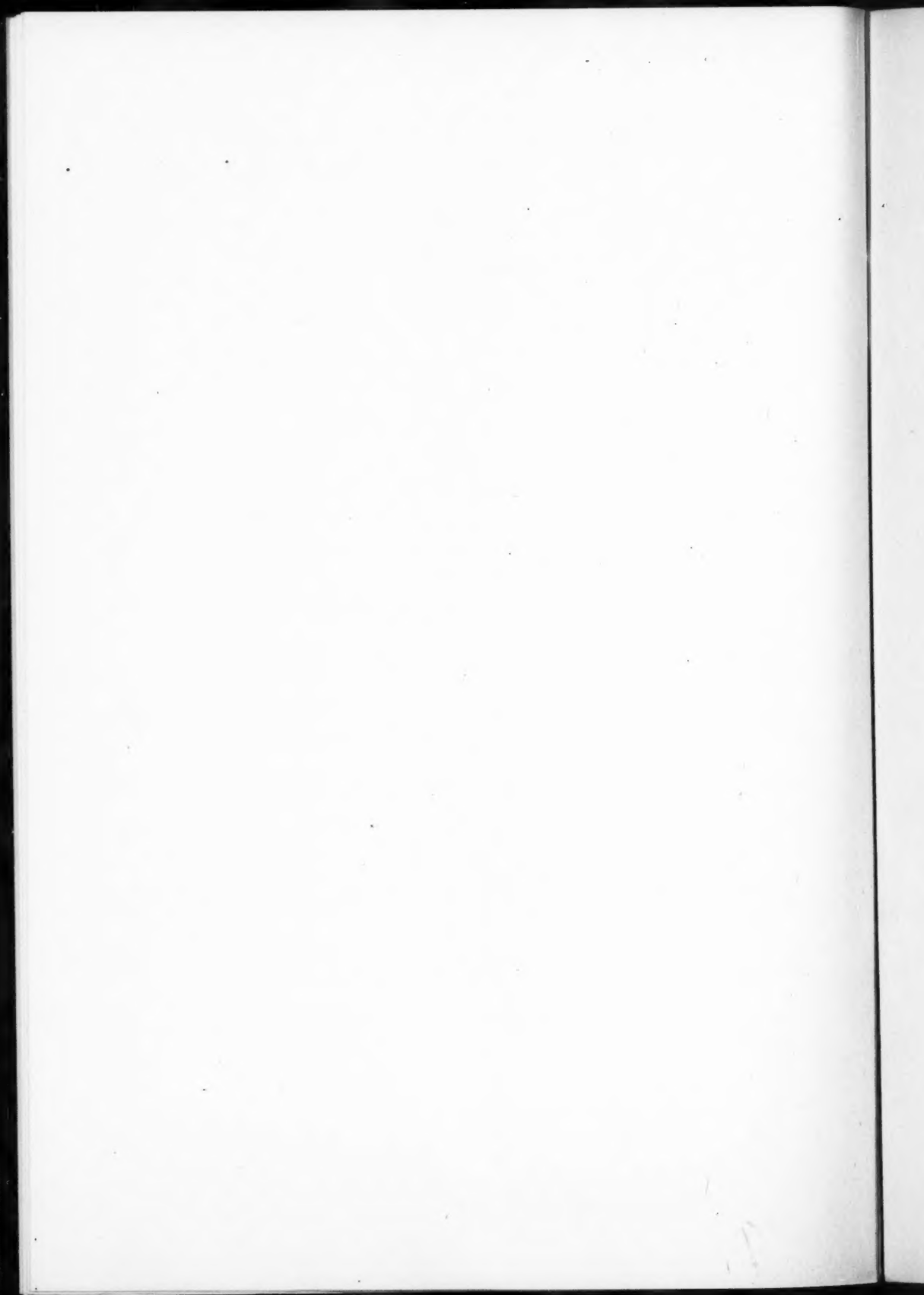
At current densities between 10 and 100% of the limiting diffusion current, the  $U^{IV}$  concentration at the electrode surface differs appreciably from that in the body of the solution. Hence, concentration polarization effects must also be considered in the interpretation of the current-potential relations in this region.

### Acknowledgment

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